

Rationale and fallacy of thermoanalytical kinetic patterns

How we model subject matter

J. Šesták

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Abstract Modeling tradition is reviewed within its historical maturity from Plato do Penrose. Metaphors in nonisothermal kinetics achieved a wide application mostly employing models derived by means of undemanding isothermal descriptions. Geometrical basis of such modeling is revised and discussed in terms of symmetrical and asymmetrical (pentagonal) schemes. The properties of interface (reaction separating line) are found decisive in all cases of heterogeneous kinetics. Application of fractal geometry is accredited, and associated formal kinetic models based on nonintegral power exponents are acknowledged. Typical erroneous beliefs are dealt with showing common kinetic misinterpretation of measured data and associated mathematical manipulability of kinetic equations. The correction of a measured DTA peak is mentioned assuming the effects of heat inertia and temperature gradients.

Keywords Nonisothermal kinetics · Reaction mechanism · Geometrical modeling · Fractals · Evaluation · Misinterpretation · DTA · Heat inertia

Devoted to the 90th birth anniversary (July 2012) of Vladimír Šatava (Prague) and also written on the occasion of passing away (October 2011 at the age 85) of Ivo Proks (Bratislava) both the foremost pioneers in the fields of thermodynamics and thermal analysis, to whom this paper is dedicated.

J. Šesták (✉)
New Technology—Research Centre in the Westbohemian
Region, West Bohemian University, Universitní 8, 30114 Pilsen,
Czech Republic
e-mail: sestak@fzu.cz

Introduction

More than a quarter century ago, I published in this journal a discussion article on kinetic evaluations [1] emphasizing various questions, which is not worth to repeat even if many of inquires have remained unanswered [2–5]. Since then, many thousands of articles were published showing that the kinetic subject has persisted to be the best cited area in thermal analysis [6]. Albeit being a doyen of such a novel [7–13] and now cross-boundary research area [14], I was proud that I was given yet another space to reevaluate and reassume my standpoints toward the thermal analysis kinetics, the subject thoroughly explored in my books [14–19]. Nonetheless, I have decided to do it in a more generalized way pointing out the pitfalls and yet unaccepted site issues to show different ways of possible and untraditional assessments even falling back upon the beliefs of Greek philosophers [18, 19].

Some philosophical thoughts on a general exercise toward mathematical models

The four basic elements *fire*, *air*, *earth*, and *water* (introduced by *Empedocles* 492–432) were the first known models and metaphors to signify the substantiality of which all subsistence is composed (i.e., *quantities* as well as interconnecting *qualities* like warmth, dryness, coldness, and humidity). They were thought to possess the integrative and structural essence *ether* or better *form* in the sense of an imperishable firmament (which in the modern world is interpreted as *in-form-ation*) [18, 19]. Today however, mathematical modeling ensues differently not only from a further approved physical existence but also from an existence that is assigned by our more cultured mental

perceptions. It is not just the precision but also the subtle sophistication and mathematical beauty of successful models that is profoundly mysterious. Mathematics is crucially concerned about *truth* and philosophers would agree that there are some other fundamental (almost absolute) concerns, namely that of *beauty* and of *good*, which exist since the Platonic geometrical world of mathematical forms [20].

The early modeling elements were first depicted by the metaphors of simple, equilateral triangles either pointing up, in order to escape like air or fire, or down, to rest like water or earth. Later *Plato* (427–347) used more explicit geometrical models spatially arranging multiple triangles, i.e., 3 triangles formed *tetrahedron* (~ fire), 8 triangles—*octahedron* (~ air), 6 squares or 12 triangles—*cube* (~ earth). Water, however, was represented by a more complex geometrical body called *icosahedra* (20 triangles, cf. Fig. 1). In Greek culture the term symmetry was interpreted as the harmony of different parts of an object. *Symmetria* (~ common measure) is composed of the prefix *sym* (~ common) and *metres* (~ measure). The Greek *Gaius Plinius Secundus* (23–79) provided the early fundament for crystallography (derived from Greek *crystallos* = piece of ice) as he gave primary rules for the plan-metric faces of crystals and their visually imagery shaping.

However, the most impressive historical treatise on crystallography was written by *Johann Kepler* (1571–1612), while residing in Prague (during 1600–1612), and was devoted to the description of snowflakes. In analyzing their numerous forms bearing a steady hexagonal symmetry, Kepler suggested a certain generalization model for the densest arrangement of rigid balls. Factually, he introduced the coordination-like number for a ball environment and declared the consistency of angles between analogical crystal planes and edges. It can be assumed that some implication of Platonian geometry was also inherent in Kepler's applications [20]. Though *Auguste Bravais* (1811–1863) was not sure that crystals are internally arranged in a repeatable manner, he mathematically modeled the 14 geometrical figures which can be spatially arranged in a periodic mode [20–22]. They can be characterized by a combination of one or more rotations and inversions in a lattice that is understood as a regular array of discrete points representing individual structural units (atoms, molecules, species, etc.), which thus appear exactly the same when viewed from any point of the array [20]. This discovery allows us to classify crystal shapes nowadays in the seven geometrically basic schemes: area and/or *space can be filled completely* and symmetrically with tiles of *three, four, and six sides*. This is close to the Platonian conceptions of geometrical bodies but excludes, however, any *pentagonal* arrangement (also involved in the early Platonic bodies) because it is not possible to fill any area

completely with its fivefold symmetry. In the early 1970s, however, *Roger Penrose* (1931–) discovered that a surface can be wholly tiled in an asymmetrical but non-repeating manner [21, 22] providing some constructions similar to the cluster structure of liquid water [23] or glassy state of non-crystalline materials (like metallic glasses), which has been for a long run in the core of attention [19], see Fig. 1.

These relations can be followed far back to history when the geometry of pentagon (and the pentagram inscribed within it) bore its high metaphysical association as explored by the Pythagoreans (after *Pythagoras* 586–506): they considered it as an emblem of perfection. It was a doctrine that all things compose and proceed from numbers and the middle number five, as being formed by the union of the odd and the first event was deemed of a peculiar value. In China, the central number five, similarly, represented the fifth additional element—the earth as the allied symbol of the great China [18, 19]. In astrology, geometrical figures kept engendering mystical and occult connotations such as with the supposed magical powers of pentagons and pentagrams. This effect lasted until recently as various occult guilds are often symbolized by five leave rose.

One consequence is the way how we fragment real-world entities into several categories [20]: *things, events, and processes*. By things, we typically mean those entities which are separable, with identifiable shapes and size, and which persist in time. Events, on the other hand, have a relatively short duration and are composed of the interactions of several things of various sizes. Processes are, in this last property, similar to events but, like things, have a relatively long duration. However, many other entities may have a transient character, such as vortices, flames, clouds, sounds, ceremonies, etc. There is an obvious difference between generic categories and particular entities because a category may be scale-thin in two different ways: generically (atoms, birds, etc.) or individually (geometrical concepts, etc.).

In the case of complex objects, there is a close relationship between their distribution over scales and a hierarchy of their structural, functional, and describable levels. We tend to assign objects of our concern into structural levels and events as well as processes into functional levels. Obvious differences of individual levels yield different descriptions, different terminologies (or languages), and eventually different disciplines. Two types of difficulty, however, emerge, one caused by our limited understanding of whether and how distinct levels of a system can directly interact and, the other, related to the communication (words) barriers developed over decades of specialization of scientific disciplines [24] (providing the urgent need for a topic *interdisciplinarity*).

One of the first mathematical theories in science that dealt with inter-level interactions was Boltzmann's statistical physics, which is related to thermodynamics and the

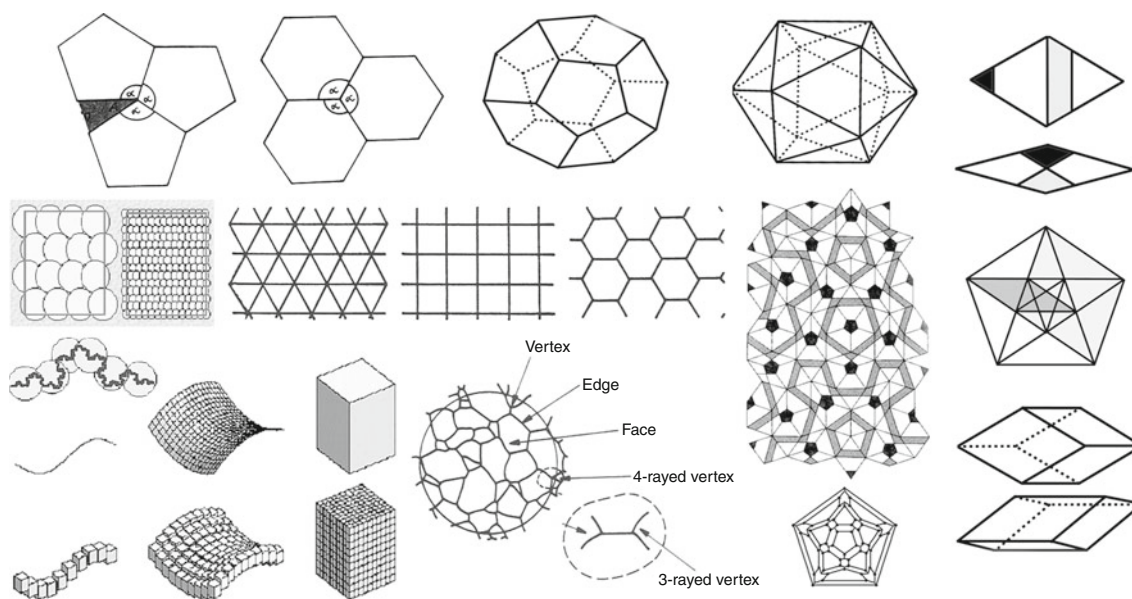


Fig. 1 Building faces (*blocks*) available for modeling. *Pentagon* and *hexagon* in the *upper row* shows the incommensurability to compose a continuous web because of uncovered/overlapping areas (*left dark*). This can only be harmonized by curving their edges or adjusting angles (five-sided \rightarrow convex and seven-sided \rightarrow concave) or employing asymmetrical tiles (*far right*). Classical symmetrical network can only be satisfied with a collection of *triangular*, *tetragonal* and *hexagonal faces* (*middle*) and their combinations. For an array of equal *balls* and/or *cubes* (even when crimped), the restrictions are faced because of a strict Euclidean dimensionality, not found, however, in any actual images, which is often characterized (or observed) by typical 2D cross-sections (*bottom right*). Irregular grain structures (*middle bottom*) possess distinctive faces, which can best be characterized by the degree of vertices (four-rayed vertex decomposing to three as a spontaneous growth occurs). Some constructions (associable, e.g., with the clustered structure of liquid water [23]) are tiling in fivefold symmetry, which were thought for long run as impossible to fill areas completely and regularly (*middle right*). *Upper right* is shown *dodecahedron* (which Plato associated with firmament) interconnecting with the larger clusters of *icosahedron* (which Plato associated with water). *Right* and *below* are visualized the *diamond*

(Penrose) basic tiles [21, 22] with a specific shape called “rhombus,” where upper thick rhomb has longer diagonal equal to the “Golden ratio” ϕ ($\phi = 1.618034$, which is related to the number 5 by formulae $(1 - \sqrt{5})/2$), fascinatingly, playing a crucial role in various aspects of natural livelihood and also man-made art constructions [20]. The thinner rhomb has his shorter diagonal equal to $1/\phi$. Both rhombs can be derived from a pentagon, which five diagonals match ϕ and which five-side structure leaves gaps when used to be continuously repeated in space. On the other hand, the rhombs can fill the surface in an asymmetrical and non-repeating manner, which is known as *continuous but non-repeating structure* (sometimes called *quasicrystals*). On expanded tiling when covering greater areas, the ratio of the quantity of thick rhombs to thin ones approaches ϕ again, and if the rhombs are marked by shadow strips, then they form the unbroken structure (*middle*) where we can localize both the chains (like polymers) and pentagons (like water clusters), where the below connectivity map shows the molecules’ orderliness within an icosahedron). Such a structuring can also be applied to a spatial distribution if the two kinds of rhombohedra are assembled to form icosahedrons matching thus the larger clusters (water again), but were never employed in the modeling of reaction solid-state species

study of collective phenomena. It succeeded in eliminating the lower (microscopic) level from the macroscopic laws by decomposing the phase space to what is considered macroscopically relevant subsets and by introducing new concepts, such as the mannered entropy principle. It requested to widely adopt the function of logarithm that was already and perpetually accustomed by nature alone (physiology, and psychology [18]). In comparison, another scaled sphere of a natural process can be mentioned here where the gradual evolution of living parts has been matured and completed in the *log/log* relations, called the *allometric* dependence, often penetrating into the kinetic evaluation methods [18, 19, 25].

Another relevant area is the study of order/disorder phenomena [18, 19], acknowledging that microscopically tiny fluctuations can be somewhat “immediately” amplified to

a macroscopic scale. What seems to be a purely random event on one level can appear to be deterministically lawful behavior on some other level. Quantum mechanics may serve as an example where the question of measurement is actually the eminent question of interpreting macroscopic images of the quantum-scale events [19]. Factually, we construct “things” on the basis of information; in resemblance we may call engines as information transducers because they transform energy without changing itself (not accounting on wearing).

Modeling roots applied in reaction kinetics

In solid-state reaction kinetics [25–40], it is convenient to postulate a thought (*gedenken*) model visualizing thus the

feedback, which is usually separated into a sequence of possible steps then trying to identify the slowest event, which is considered to be the *rate-determining process* [25]. Such models (among others, e.g., [14, 19, 26–42]) usually incorporate (often rather hypothetical) description of consequent and/or concurrent processes of interfacial chemical reactions and diffusion transport of reactants, which governs the formation of new phase (nucleation) and its consequent (crystal) growth. Such a modeling is often structured within the perception of simplified geometrical bodies, which are responsible to depict the incorporated particles, and such visualization exemplifies the reaction interfaces by *disjoining lines*. Such a derived kinetics then depends on all such physical, chemical, and geometrical events focused to the behavior of interface acting between the product and the initial reactant. Accordingly the space co-ordinates become rate-controlling elements, which create heterogeneity consequence inevitably to be incorporated. At the moment when interfaces are created, they should be identified with the underlying principle of *defects* conveniently symbolized by a pictographic contour (borderline curves) at our graphical representation (cf Fig. 1). Hence, the mathematical description turns out to be much more complicated because *no mean measure* (such as bulk concentration and temperature) but the *spot/site/defect assessment* (extent of phase interface or gradients) *carries out the most considerable information* undertaking thus the posture of true rate-controlling process/execute associable with the reaction progress (cf. Fig. 1), not omitting the delivery task of reaction species moving to and/or from reaction boundary.

Early in 1950s, Smith [43, 44] already proposed a classical approach emphasizing “normal grain growth result for the interaction between the topological requirements of space-filing and the geometrical needs of surface tension equilibrium.” We can distinguish that in both 2D and 3D (dimensional) arrangements, the structure consists of vertices joined by edges (sides), which surround faces and in the 3D case, the faces surround cells, see Fig. 1. The cells, faces, edges, and vertices of any cellular structure obey the conservation law (Euler’s equation), i.e., $F - E + V = 1$ (for 2D plane) and $F - E - C + V = 1$ (for 3D space). Here C , E , F , and V are, respectively, the number of cells, edges, faces, and vertices. Moreover, the number of edges joined to a given vertex settles its coordination number, z . For a topologically stable structure, i.e., for those in which the topological properties are unchanged by any small deformation, $z = 3$ (for 2D) and $z = 4$ (for 3D), is legitimate everywhere. This can be best illustrated for 2D structure by a four-rayed vertex, which will tend to be unstable decomposing into two vertices, each of three-rays, which process is often termed as *neighbor-switching*. For a 2D structure, in which all boundaries have the same surface

tension, the equilibrium angles at a vertex are 120° . The tetrahedral angle at $109^\circ 28'$ is the equilibrium angle at a four-edged vertex in 3D having six 2D faces.

The grain growth in 2D is inevitable unless a structure consists of an absolutely regular array of hexagons. If even 1 five-sided polygon is introduced and balanced by a seven-sided one then the sides of the grains must become *curved* to maintain 120° angles at the vertices. Grain boundary migration then tends to occur because of the curvature maneuver reducing boundary surface tension so that any grain with the number of edges above six will tend to grow because of concave sides and below six will incline to shrink because of convex sides.

It is clear that any reaction rate, particularly at the beginning of its “acting-ion-exchange,” must depend upon the size of the solid grains which undergo transformation (growth or dissolution). Reaction rate, r^- , should thus be inversely proportional to the particle size, r , in the form of a certain power law: $r^- = r^{D_r-3}$, where D_r is the *characteristic reaction dimension*, which can be allied with a *nonintegral fractal* [45–48]. It is obvious that a mere use of strict integral dimensions, typically r^1 and r^2 , would be an apparent oversimplification. Moreover, we have to imagine that the initial rate is directly proportional to the extent (true availability) of “ready-to-react” surface and/or interface as well as to its coarseness (i.e., roughness as a kind of another characteristic with a non-integral dimension, again). It seems that such a concept can be discriminated as rather useful to describe the responding behavior of a reacting object toward the reaction impact characterized by *fractal dimension*. It recounts in *-self* summing all events occurring during the overall heterogeneous process. There, however, is not a regular polyhedron with plane sides subsisting exactly tetrahedral (angle $109^\circ 28'$ between the edges). The nearest approach to space filling by a regular plane-sided polyhedron in 3D is obtained by the Kelvin ideal tetracaidecahedra spaced on a body-centered cubic lattice. Even then, the boundaries must become curved to assure equilibrium at the vertices so that a grain growth is likely to occur. It can be even illustrated by beer frost, which can be of two kinds: at-once draft beer with more interfacial fluid possessions (enabling mutual bubble slipping) and the already aged beer with a more rigid interfacial structure (\sim “dry” hexagonal-like make up). Apparently, both are unlike in experts’ taste, being capable, however, to self-adjust by boundary migration and gas permeation through the cell membranes to equalize pressure of adjacent bubbles.

The most common kinetic models are associated with the shrinking core of a globular particle, which maintains a *sharp* reaction boundary [26–36]. Using a simple geometrical representation, the reacting system can be classified as a set of spheres [18, 19] where each reaction interface is

represented by characteristic curve. We assume that the initial reactants' aggregation must be reached by (assumingly) well-distributed (homogenization of reacting) components (often through various transporting means) otherwise possibly initiating certain *self-organization* [18, 19]. Any of such created interfacial (separating) layers, y , endures thus the role of a *kinetic impedance*, and the slower of the two associated elementary processes, i.e., *diffusion* to/from acting along with the chemical *interface*, then becomes the *rate-controlling* process [18–42, 49–51] responsible for the *over-all* reaction progression. We may indicate that that the above discussed kind of “*as-belief*” models depict both the ideal situation of only single-reaction controlling mode as well as a rigid spherical representation for *all* reacting particles. Though this simplification has no any investigational authorization, such a theoretical fashion sometimes (and from time to time even routinely) provides a surprisingly good fitting for thermoanalytical data kinetics ignoring a common inspection misfit often adjusted by means of simultaneously accomplished direct observations (such as microscopy). Rationalized approach can be accomplished when assuming a certain model coincidence for improved geometrical fit incorporating thus some additional symmetry features such as a regularity adjustment of pattern-similar-bodies (globe \leftrightarrow prism \leftrightarrow cube \leftrightarrow block \leftrightarrow hexahedral \leftrightarrow dodecahedral \leftrightarrow etc.). It somehow helps us to authorize the relation truthfulness and applicability of such (*oversimplified*) models when put into operation on more cogent (*irregular*) structures, which we often decline, or at least, are anxious to observe. Even symmetry generalization does not facilitate above modeling to the full-scale matching of real morphologies (customarily witnessed in practice).

In our kinetic practice, we can either survive with a simplified model-free description using a “blank” modeling pattern (as below shown *SB equation*) or we ought to adapt another philosophy of modeling whichever reaction mechanisms, learning how to employ more complex mathematics and/or providing a range of functions instead of single numerical values (typically activation energies often pointlessly précised to decimal places). This tactic, however, may auxiliary interfere within the limiting cases of experimental setup: either by diminishing the sample size to a certain threshold (thus being incapable of distinguishing the measured response of bulk behavior from that of sample surface) or by accelerating the imposed temperature changes ($\gg \phi$) probably getting in touch with an effect analogous to the *uncertainty principle* (unable to correspondingly determine each one of the independently measured parameters with an adequate precision, i.e., temperature and/or and its change—heat flux). Therefore, the future development of thermal analysis may become different than that we presuppose today.

Use of yet atypical fractal geometry

Always existing perturbations on the reaction interface can be imagined to encounter a driving force to accelerate growth that is usually expressed by the negative value of the first derivative of the Gibbs energy change, ΔG , with respect to the distance, r . For small super-heating/cooling, we can still adopt the concept of constancy of the first derivatives, so that $d\Delta G$ equals to the product of the entropy change, ΔS , and the temperature gradient, ΔT , which is the difference between the thermodynamic temperature gradient (associated with transformation) and the heat-imposed gradient at the reaction interface as a consequence of external and internal heat fluxes. Because ΔS is often negative, a positive driving force will exist to allow perturbations to grow, only if ΔT is positive. This pseudo-thermodynamic approach gives the same result as that deduced from the concept of zone constitutional undercooling [52, 53], and its analysis is important for the manufacturing advanced nano-materials [54–57] such as fine-metals, nano-composed assets, formation of quantum low-dimensional possessions (dots), composite whiskers, tailored textured configurations, and growth of oriented biological structures.

The physical–geometrical models also neglect other important factors such as interfacial energy (immediate curvature, capillarity, tensions, nano-grains radius [54–57]), and particularly undistinguish internal and external transports of heat and mass (to and from the localized reaction boundary) resulting in a breakdown of smooth (planar) reacting interface [19], which, at the process terminations, are anyhow responsible for complex product topology [52, 53]. Various activated disturbances are often amplified until a marked difference in the progress of the tips and depressions of the perturbed reacting interface occurs, making the image of resultant structures irregular and indefinable [19, 52–54, 58]. It creates difficulties in the correlation of traditional morphology observations with anticipated structures, becoming rather different from the originally assumed (simple, planar, 3D, etc.) geometry. Depending on the directional growth conditions, the so-called dendrites (from the Greek *dendros* = tree) develop their arms of various orders and trunks of different spacings because of the locally uneven conditions of heat supply. This process is well known in not only metallurgy (quenching and casting of alloys [52, 53, 58], water, and weather precipitates (such as snow-flakes formation or crystallization of water in plants) but also for less frequent types of other precipitation, crystallization, and decomposition processes associated with dissipation of heat, fluids, etc.

First, we should notice that there are sometimes fussy effects of particle radius, r , encompassing a wide range of

reacting compacts. Besides affecting measurable point of phase changes [55–57], the most of the derived model relations stay either for a simply reciprocity ($\sim 1/r$, if the whole reacting surface is exposed to ongoing chemical events) or for the inversely proportional square ($\sim 1/r^2$, if the diffusion across the changing width of reactant/product layer became decisive). It is clear that for a real instance, we can imagine such a situation when neither of these two limiting cases is unailing so that the relation $1/r^n$ becomes effective, and a new non-integral power exponent, n , comes into view falling to the *fractal region* $1 \leq n \leq 2$. It is somehow similar to the case of heat transfer across the layer d , which can similarly fall in between two optimal cases limited by $1/d$ and $1/d^2$. The associated cooling rate ϕ is essentially influenced by the heat transfer coefficient, Λ , and the thickness of cooled sample, d , and relatively less by its actual temperature, T . At the condition of ideal cooling, where we assume infinitely high coefficient of heat transfer, the cooling rate is proportional to $1/d^2$, while for the Newtonian cooling controlled by the character of phase boundary, ϕ correlates to $1/d$, only. In practice, we may adopt the power relation $\phi = 1/d^n$ (where n is a nonintegral experimental constant $1 \leq n \leq 2$).

We can presuppose that transport properties, because of fractal nature of percolation changes, incorporate into the physical laws. For an enough randomly diluted system, we can even admit that the localized modes occur for larger reacting frequencies, which can be introduced on basis of bizarrely called *fractons* [18, 59]. Inherent state density then shows an anomalous frequency behavior and, again, the power laws can characterize their dynamic properties. On fractal conductors, for example, the density is proportional to L^d and approaches zero for $L \rightarrow \infty$. If we increase L , we increase the size of the non-conducting holes, at the same time decreasing the conductivity, σ , which, because of self-similarity, decreases on all length scales, leading to the power law dependence defining the critical exponent, μ , as $\sigma \sim L^{-\mu}$. Owing to the presence of holes, bottlenecks, and dangling ends, the diffusion is also slowed down on all length scales. Assuming the common example of “*random walker*” [60–63] and its probability to stay in place (using the standard relation, $x^2(t) = 2dDt$, where D is the diffusion constant and d is the dimension of lattice), the classical Fick Law loses its orthodox validity. Instead, the mean square displacement is described by more general power law: $x^2(t) \cong t^{2/d_w}$, where the new exponent, d_w , is always greater than two. Both exponents can be related through the Einstein relation, $\sigma = enD/(k_B T)$, where e and n denote, respectively, the charge and density of mobile particles, and k_B is a rate constant. As a result, $d_w = d' - d + 2 + \mu$, where d' can be substituted by the ratio relation, $\log 3/\log 2$, so that d_w becomes proportional to

$\log 5/\log 2$, which, however, is not so easy to ascertain in the standard integer-like cases.

It is widely shown [60–63] that many dynamic systems can *regularly produce a chaotic behavior*. One set of associated problems for us is the investigative concern in the direction of a difference equation called *logistic mapping* obviously being the quadratic transformation, which comes in different forms, typical succession as $x \rightarrow a x(1 - x)$. This name sounds a little peculiar in modern science as its origin subsisted in economics from which it gives us the term logistic to describe any type of a planning process. It derives from the consideration of a whole class of problems in which these two factors control the size of a changing population, x varying between 0 and 1. This population passes through a succession of generations, labeled by the suffix n , and so we denote the population in the n th generation by x_n . There is a birth process in which the number of populated species (nuclei, insects, and even people) would deplete resources, and prevent survival of them all. There is a negative depletion term proportional to the square of the population. Putting these together, we have the nonlinear difference equation. By defining the iteration as $x_{n+1} = a x_n(1 - x_n)$, we can illustrate the process graphically upon the superimposed parabola (x^2) and straight line (x) in the interval $0 \leq x \leq 1$ [18]. We can arrive to the two types of iterations by adjusting both the initial point, x_0 , and the multiplying coefficient, a . It can either exhibit a sensitive-irregular pattern or non-sensitively stable behavior. Very important phenomenon is thus sensitivity, which either can magnify even the smallest error or dump the larger errors, if the system is finally localized in the stable state. This behavior is called the *sensitive dependence on initial conditions* and is central to the problematic of chaos [18, 49, 60–63], though it does not automatically lead to disorder.

The crucial difference between the discrete logistic system and its continuous derivative-like counterpart subsists in the fact that it is plainly impossible for the dynamics of the differential equation to behave chaotic. The reason is that in the 1D system, no two trajectories, for the limit $\Delta t \rightarrow 0$, can cross each other, thus typically converging to a point or escaping to infinity, which, however, is not a general consensus in 3D system often displaying chaos. These types of differential equations are the most important tools for modeling straightforward (“vector”) processes in physics and chemistry, though, no single particular analytic solution is regularly available. The associated relationship can be transposable to write the form of a common kinetic equation: $d\alpha/dt \cong \alpha(1 - \alpha)$, where α can be the normalized extent of chemical conversion. Factually, this is a well-known form of Prout-Tompkins’ self-catalyzed kinetic model [64, 65] naturally

related to various aspects of contradictory chemical reactivity. However, life in the real science is not simple and almost in any physical–chemical system, the state cannot be described by a single variable or equation characterized by an integral power exponent ($=1$), as shown in detail in the previous paragraph. Therefore, it was obvious that for generalized purposes of chemical kinetics, this logistic-like equation has got to be completed by the non-integral exponents, m and n , as completed in the advanced form of Šesták–Berggren (SB) equation [66–69] $d\alpha/dt \cong \alpha^m(1 - \alpha)^n$. The involvement of reactants (α) and products ($1 - \alpha$) is attuned to their actual chemical transience (m) and fertility (n), which is timely adjusted by this type of power-law [18, 19].

Yerofeev [70] has already shown that if a solid is involved with acting interfaces, the formation and growth of nuclei are describable by the above SB equation with $m = 2/3$ and $n = 2/3$. It may include certain extension and correlation, for example, for: $m = 1/2, 2/3, 3/4, 4/5, \dots$, and 1 : $n = 0.774, 0.7, 0.664, 0.642, \dots$, and 0.556 , respectively. It was shown [32, 33, 66–68] that such a two-parameter model retains its physical meaning only for $m \leq 1$ which can be even correlated with the classical nucleation-growth equation (often abbreviated as JMAK) staying factually the special case of SB equation (when approximating $\{\ln(1 - \alpha)\}^p$ through expansion by α^m [18, 19]). The increasing value of the exponent m indicates “mortality”—a more important role of the precipitated phase on the overall kinetics. It also appears that a higher value of the second exponent ($n > 1$) indicates increasing reaction complexity; however, the temptation to relate the values of m and n to a specific reaction mechanism can be doubtful and should be avoided without complementary measurements [18, 19]. Besides Malek shown [71, 72] that there exists a relationship between the JMAK robust exponents $r = 0 \rightarrow 1.5 \rightarrow 2 \rightarrow 3$ and SB exponents keeping on the respective values $m-n = 0-1 \rightarrow 0.35-0.88 \rightarrow 0.54-0.83 \rightarrow 0.72-0.76$. Nevertheless the best interpretation depicts n and m as mere fractals without any correlation to a reaction mechanism.

Manipulability of the kinetic equation

Chemical kinetics is based on the experimentally verified assumption that the reaction rate r^{\rightarrow} , based on *degree of conversion* α , is signified by time (t) derivative $d\alpha/dt$, which is a function, f , of the state alone, i.e., $d\alpha/dt \cong f(\alpha, T)$. The state dynamics of a studied system is characterized by the mean and dimensionless measure of reaction progress (α) [18–42, 49–51]. The long-lasting practice has accredited a routine in which the function $f(\alpha, T)$ is divided into the two mutually independent functions, $k(T)$ and $f(\alpha)$. Using this traditional postulation, the appropriate constitutional

approach to inaugurate the desired constitutive equation [73, 75] depicts a principal form of the product of two separate functions, i.e., the *rate constant* $k(T)$, dependent solely on the temperature, T , and the mathematical portrayal-model of the *reaction mechanism*, $f(\alpha)$, reliant on the variation of the degree of conversion, only [18, 19, 74]. It may be complicated by interference of a changing equilibrium background in which α became a product of two kinetic λ and equilibrium λ_{eq} degrees [75] ($\alpha = \lambda/\lambda_{\text{eq}}$). The degree of conversion may eventually involve multiple kinetic degrees (such as simultaneous phase separation [76] etc.) and may also become pressure dependent, etc.

For a mathematical treatment, we have any number of possibilities of mathematical manipulations: we can adjust modification of either term: $d\alpha/dt$ ($\sim \alpha'$), $f(\alpha)$ or $k(T)$. We are all familiar that the derivative can possess only an integer order (1,2,3...), which is a common language for formulating and analyzing many laws of physics. In accordance with above discussion, even the calculus of fractional derivatives [77, 78] may become adequate to be employed for kinetic applications (factually being an old technique selected by *Gottfried von Leibnitz* already in 1695), i.e., $d\alpha^x/dt^y$ (explicitly for a case of $x = 1/2$ it makes equal to $\alpha\sqrt{(d\alpha/dt)}$ [77, 78]). It has already affected the classically derived Fick law of diffusion, showing certain exceptions, which is termed as *strange kinetics* [79]. It is based on the portrayal of a random walker concept (see above) and on an unconventional distribution of functions. In standard kinetics, however, fractional derivatives did not come into sight as yet which does not exclude a chance that in future a mathematically based application would surface conquering its apparent controversy embedded nowadays. Worth noting is another curiosity associated with derivatives, which appeared when the constitutive rate $d\alpha/dt$ was incorrectly treated as a multiple of two partial terms, i.e., temperature $(d\alpha/dt)_T$ and time $(d\alpha/dt)_t$ dependent [2, 3, 73–75]. This implication created a long-lasting anarchy in the scientific literature fortunately clarified in time [18, 19, 73] though some strange commentary issues keeps persistent until today.

A long-lasting kinetic practice employs both functions $k(T)$ and $f(\alpha)$ after their analytic implementation. Traditional approach habitually employs the *Arrhenius exponential constant* because kineticists believes [19, 80, 81] in the exponential law of energy distribution, $k(T) = A \exp(-E/RT)$, derived by Arrhenius for the stochastic process of evaporation (and approved by Boltzmann statistics). However, experimentalists often think it can be proved mathematically while the mathematicians believe it has been established by observations. Parameter E is the so-called activation energy identified as the energy barrier (or threshold) that must be surmounted to enable the occurrence of the bond redistribution steps required to convert reactants to products. The pre-exponential term, or *frequency factor*,

A, provides a measure of the frequency of occurrence of the reaction situation. Although the Arrhenius equation has been widely (and often successfully) applied to innumerable solid-state reactions, its use factually lacks a theoretical justification (merely acknowledged in homogeneous systems) because the energy distribution, particularly among the immobilized constituents of crystalline reactants, may not be adequately represented by the *Maxwell–Boltzmann* equation. The interracially reacting species, however, encompass a certain degree of freedom to adjust their energy distribution along the surface reaction zone affecting the energy sharing in reactive sites (reaction interfacial contact), moreover exaggerated by strain (between the differently juxtaposed networks), nonstoichiometry, defects, catalytic activity of newborn sites, irreversible re-crystallization, or perhaps even by local volatilization (if not accounting for the thickness of such a reacting zone contoured by local heat and mass fluxes across and along the interfaces). An alternative framework for this theory of solid-state decompositions [82] is available through the so-called L'vov's [83] congruent dissociative vaporization (CDV) mechanism. Here the super-saturation (S) of the vapor of the low-volatility component at the instant of decomposition is related through a transfer parameter τ by proportionality ($\tau \cong 0.351 \log \log S + 0.017$). However, this unusual (doubly logarithmic) relationship between τ and S may become a key point in understanding the mechanism of energy transfer in condensation (for low volatility component distribution between reactant and product solids) depending on the ratio characterized by the τ -coefficient.

When $f(\alpha)$ function is routinely modeled on basis of simplified physical–geometrical assumptions [14–19, 25–42], the direct application of the basic differential equation is straightforward. However, the *differential mode* of evaluation can even provide a better matching up with the true experimental conditions when the actual non-uniform heating and factual temperatures are considered. In such a case, we ought to introduce the second derivatives, T'' and α'' leading to a more complex equation correlating $\alpha'' T^2 / \alpha' T'$ with $df(\alpha)/d\alpha / f(\alpha) \{T^2 \alpha' / T'\} + E/R$. It occurs that it is almost impossible to evaluate this relation with a satisfactory precision because of its extreme sensitivity to noise, particularly affecting the second derivatives (as well as heat flow changes, q'' , see below) A more convenient and rather popular method of kinetic data analysis is based on expressing the maximum value (index *max*) on the dependence of α' versus T , for which it holds, $\alpha'' = 0 = \alpha'_{\max} \{E/RT_{\max} / Z / \phi \exp(-E/RT_{\max}) df(\alpha)/d\alpha\}$. The result provides simple but rather useful dependence, often called Kissinger plot (known since 1959 [84]), which in various modifications and reproves shows the basic relation between the ratio of heating rate ϕ and the peak maximum temperature T_m along with the activation energy E .

The so-called integral methods of evaluation [14, 18, 19] have become recently more widespread. They are based on a modified, integrated form of the function $f(\alpha)$, which is determined by the following relation, $g(\alpha) = \int_0^\alpha d\alpha / f(\alpha)$ and rather intricate integration of the rate constant $\int_{T_0}^T k(T) dT / \phi = (AE) / (\phi R) \exp(-E/RT) \pi(x) / x$ where ϕ is the constant heating rate applied, $\pi(x)$ is an approximation term of the temperature integral (a common target of numerous publications [42, 85]). In many cases its value is simplified and even neglected, which can be visualized by simple withdrawal in front of the integral, namely: constant $\int k(T) dt \approx k(T) \int dt$. This mathematical handling is habitually obscured within complicated mathematics but got involved in the nonisothermal derivation mode of traditional nucleation-growth (JMAYK) equations [76, 86, 87].

It is evident that the derivation increases discrimination introducing, however, too high sensitivity to experimental noise and, on contrary, the integration decreases noise sensitivity but launches a lower indifference toward different $f(\alpha)$ -resolution (*discriminability*) [18, 19]. In the history of kinetic appraisal, there appeared curiosity when three similar but also disparate ways of evaluation seeks for a linear correlation of the logarithmic form of kinetic model function $\ln g(\alpha)$ either $\ln T$, T and $1/T$; all making available a equivalent outlook for the corresponding values of activation energies, E , evaluated from the slope of respective plots. Such an inbuilt disparity is caused by the different approximation of $\pi(x)$ function applied differing in the multiplication parameter, which by itself well indicates a certain extent of inherent inexactness of such a kind of kinetic evaluation. A better insight of this inquisitiveness was provided by the use of an asymptotic expansion [88] of a series with a dimensionless parameter replacing E_{app} . It revealed that the $\ln g(\alpha)$ versus $1/T$ plot is twice as good as that of the former two dependencies. In this way, we can also substantiate the numerical results of several authors who found that the plain dependence of $\ln g(\alpha)$ versus T yields E with an error of at least 15%, whereas the $1/T$ plot can decrease this error by half.

Important practical correlations were adjusted for variously interpreted E [15, 19]. For example, a rather sophisticated correlation provides interrelation between the experimental activation energy, E_{DTA} , and those for shear viscosity, E_η , on the basis of the relative constant width of glass formation interval, T_g (i.e., difference between the onset and outset temperatures). It reveals a rough temperature dependence of the logarithm of shear viscosity η on the measured temperature, T , using the simple relation $\log \eta = 11.3 + \{4.8/2.3 \Delta(1/T_g)\}(1/T - 1/T_g)$ [89] detailed discussion of which is beyond the scope of this text.

The basic JMAYK equation reveals that the apparent (overall) values of activation energies, E_{app} (particularly

being the center of interest when determined on the basis of DTA/DSC measurements, E_{DTA} can be conveniently correlated to the partial activation energies [14, 18, 19, 42, 90, 91] of nucleation, E_{N} , growth, E_{G} , and/or diffusion, E_{D} employing a simple relation $E_{\text{app}} = (a E_{\text{N}} + b E_{\text{G}}) / (a + b)$ where a and b are characteristic multiplying constants providing that the denominator $(a + b)$ equals to the robust power exponent of the integral form of JMAYK equation [18, 19, 71, 72], and the value b corresponds to 1 or 1/2 related to the movement of growth front controlled by either chemical reaction (1) or diffusion (1/2). Moreover, the coefficients d and b are associable with the nucleation velocity and the growth dimension, respectively. I am proud to mention that I was the first person pointing out such a likelihood [90], though it may become a persuasive but often misleading tool in an effortless interpretation of reaction mechanism.

The above evaluation quandary can be eased upon the application of the sample controlled thermal analysis (SCTA) method or constant rate thermal analysis (CRTA), where it is not monitoring the constant increase of temperature but the constant rate of reaction ($\alpha' = d\alpha/dt = \text{constant}$) [92–94]. It, however, does not help in avoiding undesired mathematical interrelation between the pre-exponential factor A and the activation energy E in the standard exponential law (the so-called kinetic compensation effect—KCE) [95–98]. A complementary help can be achieved when employing simultaneous experimental techniques such as optical microscopy [99–101] or dilatometry [100, 101].

Only plausible aid is introducing a novel kind of rate constant [102] or treating the kinetics in the novel so-called model-free or nonparametric mod of evaluation [103–106] where the traditional functions $k(T)$ and $f(\alpha)$ are replaced by a joint function $f(\alpha, T)$, thus going back to the roots of kinetic evaluations. It may avoid customary exploitation in terms of ill-reputed and almost religious constants, mostly linked with the activation energies that never express the ease of reaction (to be desirably related to the reactivity as a kind of “tolerance” and to the reaction mechanism as a kind of “annexation”).

In conclusion, I would like to draw attention to yet other outstanding issues that we outlined 40 years ago when interpreting a compositional case of a measured DTA peak assuming the inherent effect of *heat inertia* [107–110] (i.e., the term $d\Delta T_{\text{DTA}}/dt$ which is a standard part of the DTA and/or heat-flux-DSC equation [14, 19, 107, 108, 110]). Such an expediency rather of great importance has remained overlooked in most books [30, 31, 112–114] (with few exceptions [18, 19, 115]). Our recent studies [111] indicate that this feature is not a fiction but bears a true consequential impact arising from the real process of heat transfer (q) which has the greatest impact for moments

where the heat flux is immediately changed ($\ll q''$). Our numerical stimulations [111] show that the heat inertia effect is even amplified because of such temperature gradients affecting thus the shape of corrected DTA peak. Associated mistakenness is not reduced by shrinking the sample size to micro-level [111]. It is questionable whether such difference between the measured (as-determined) and authentic (as-rectified) DTA peak impinges on the supplementary derived data especially when calculating the reaction progress (α) from the enveloped peak areas and/or on the kinetic data evaluated from the shift of peak apexes [84] or fractionally determined at successive α 's. It is an open sphere for further examination and DTA evaluation scrutiny together with hidden and yet unidentified problems [111] brought about by lessening the sample micro-size [19, 55–57] and escalating the employed heating/cooling rates [19, 52–54].

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